

SYNTHESIS GROWTH AND PROPERTIES OF AN ORGANIC NONLINEAR OPTICAL CRYSTAL L HISTIDINIUM MALEATE (LHM)

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ABSTRACT

The objective of this study is to grow and to characterize the L- Histidinium Maleate (LHM) crystal and to learn its suitability in modern Non-Linear Optics. This organic crystal grown by slow evaporation method has shown amazing optical performances and satisfactory spectral impressions in electronic and vibrational spectra. The Powder X-Ray Diffraction (PXRD) pattern confirmed the crystallinity of the synthesized LHM crystal. The Second Harmonic Generation (SHG) of LHM confirmed its Non-Linear Optical (NLO) performance.

Keywords : X-Ray Diffraction, Thermal Property, NLO material

1. Introduction

The synthesis of new organic crystals having nonlinear optical property is essential for chemistry and physics scholars due to their potential applications in the area of telecommunications, signal processing, optical switching and data storage technology [1-5].

L-Histidine possesses imidazole moiety and high optical nonlinearity compared to other amino acids [6-8]. In the present study, a systematic examination has been carried out on the synthesis and growth of L-Histidinium Maleate. The grown crystal was subjected to various characterization techniques, such as single crystal and powder X-ray diffraction, optical absorption, Fourier Transform Infrared Spectroscopy, Conductivity, Photoluminescence and Second harmonic generation test.

2.Experimental

An equimolar quantity of L-Histidine and maleic acid was dissolved in a mixed solvent of ethanol and water and the solution was stirred well for about 1h using a magnetic stirrer to ensure homogeneous concentration over entire volume of the solution. The prepared solution was allowed to evaporate at room temperature. The quality of the material was improved by successive recrystallization processes.

Transparent crystals were harvested in a period of 12 days. The photograph of the as-grown crystals of L-Histidinium Maleate is shown in Fig.1.



Fig.1 As grown single crystals of L-Histidinium Maleate

3 Results and Discussion

3.1 Single Crystal X-Ray Diffraction

The single crystal X-ray diffraction has been carried out using Enraf-Nonius CAD-4 diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). L-Histidinium Maleate crystal belongs to the triclinic system. The cell parameters are $a = 7.22 \text{ \AA}$, $b = 9.89 \text{ \AA}$, $c = 12.94 \text{ \AA}$ and volume $V = 845 \text{ \AA}^3$,

3.2 Powder X-Ray Diffraction

LHM was subjected to powder X-ray diffraction analysis using a Reich-Seifert X-ray diffractometer with CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation. The sample was scanned over the range of 10° - 60° at a rate of $1^\circ/\text{min}$. The X-ray diffraction pattern of L-Histidinium Maleate is shown in Fig.2. The X-ray diffraction peaks were indexed for the lattice and the prominent peaks obtained from the powder parameters X-ray diffraction confirm the crystallinity of the grown crystals.

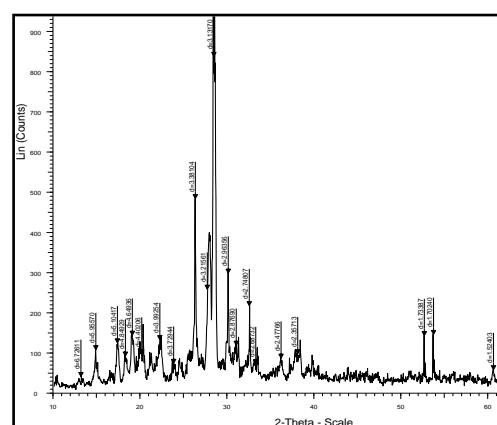


Fig. 2 X-ray Diffraction pattern of L-Histidinium Maleate

3.3 UV-VIS-NIR Absorption Spectrum

The grown single crystal was subjected to UV-vis-NIR studies at room temperature in the wavelength range from 200 to 1000 nm using a Shimadzu UV-vis spectrophotometer and the recorded spectrum is shown in Fig.3. From the absorption spectrum, it was found that the lower cut-off wavelength is 285 nm. The crystal is found to be transparent in the region of 400–800 nm which is an essential parameter for frequency doubling applications [9].

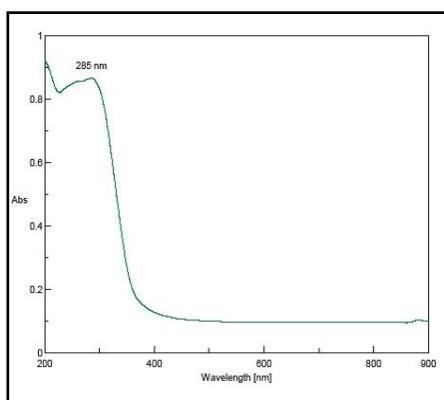


Fig. 3 Optical Absorption Spectrum of L-Histidinium Maleate

3.4 FTIR Analysis

The FTIR spectrum of L-Histidinium Maleate was recorded using PerkinElmer Spectrophotometer in the mid IR region of 4000 cm⁻¹ to 600 cm⁻¹ by KBr pellet technique is given in Fig.4. A peak observed at 3374 cm⁻¹ corresponds to the NH₂ stretching vibration. The broad absorption band in the region of 3055 cm⁻¹ is due the O-H stretching vibration. A band at 2871 cm⁻¹ is due to the C-H functional group stretching of the LHM molecule. C=O asymmetric stretching vibrations of LHM is observed in the region of 1704 cm⁻¹.

Symmetric stretching vibrations of C=O functional group is observed in the region of 1564 cm⁻¹. Bands observed in the region of 1454 cm⁻¹ and 1429 cm⁻¹ are due to H-O-H deformations [10]. FTIR absorptions at 1350 cm⁻¹ and 1254 cm⁻¹ are the cause of asymmetric and symmetric C-N stretching vibrations. The C-O functional groups of LHM shows IR absorptions at 1214 cm⁻¹ and 1176 cm⁻¹. The absorption due to in-plane bending of C-N functional group in FTIR spectrum is seen at 1082 cm⁻¹. The in-plane bending of C-O is observed at 976 cm⁻¹. A band at 880 cm⁻¹ is due to the absorption of C-H in plane bending. The bands at 780 cm⁻¹, 700 cm⁻¹ and 630 cm⁻¹ are due the out-of plane deformations of C-O and C-H functional groups.

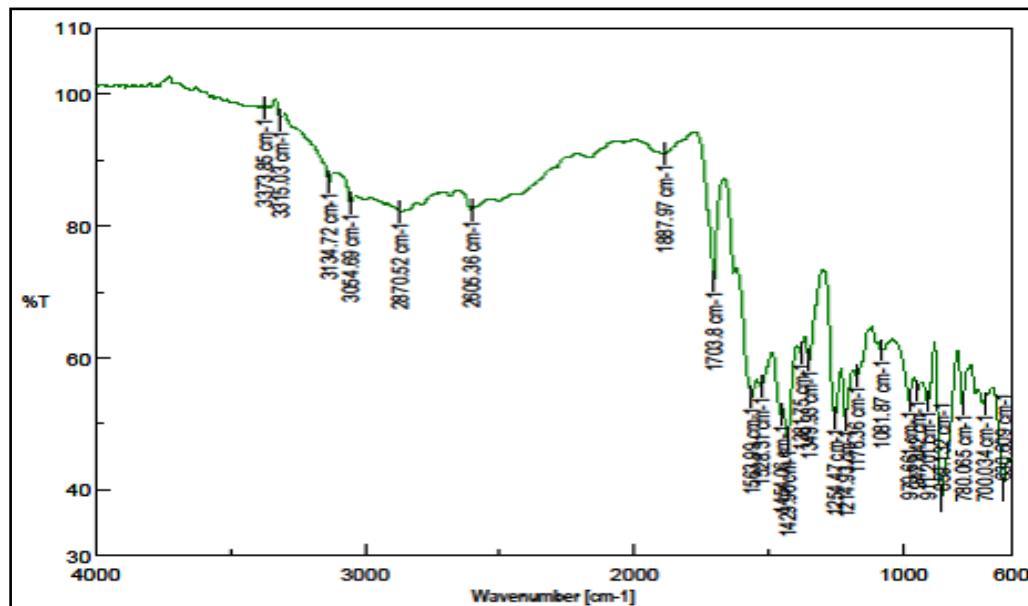


Fig. 4 FTIR Spectrum of L-Histidinium Maleate

3.5 Thermal Analysis

The thermogravimetric (TG) and differential thermal analyses (DTA) provide information about phase transition, water of crystallization and different stages of decomposition of the crystal system. The thermal behavior of the material was studied using ZETZSCH-Geratebau GmbH thermal analyzer. The sample was heated in a nitrogen atmosphere in an alumina crucible at the rate of

100°C/min. The TGA and DTA thermogram of the grown crystal is shown in Fig. 5.

TGA shows that the material starts to decompose at 101°C followed by weight loss at 132°C, 185°C and 205°C. The weight losses are due to the volatility of the residual organic functional groups. A sharp endothermic peak at 101.6°C indicates the melting point of the material. From TG-DTA it was found that the material is thermally stable up to 101.6°C.

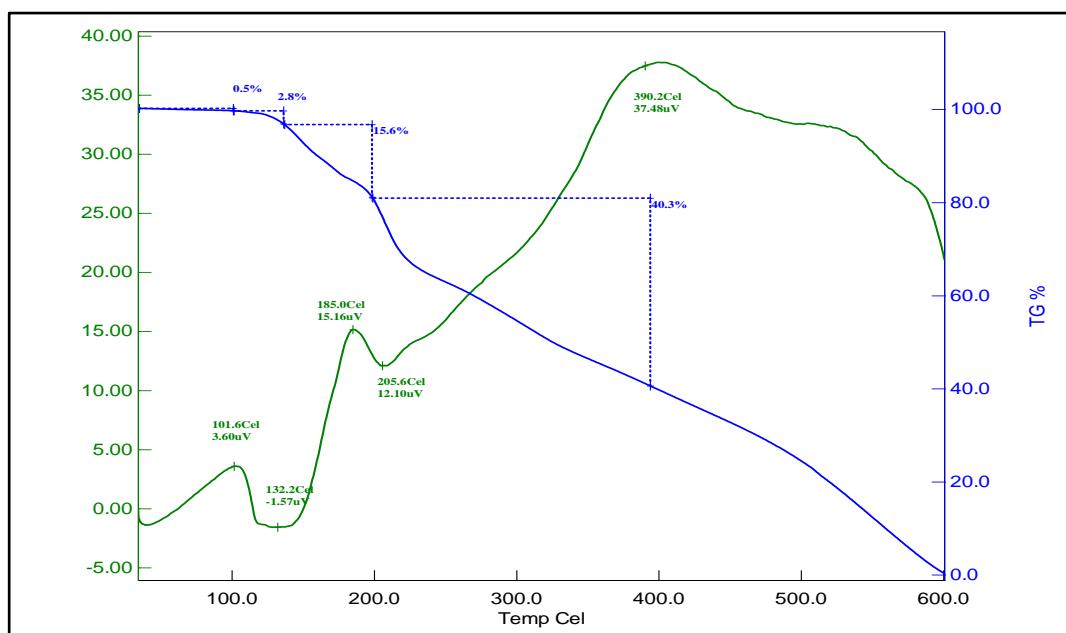


Fig.5 TGA and DTA thermogram of L-Histidinium Maleate

3.6 Photoconductivity Measurement

Photoconductivity plot of the L-Histidinium Maleate crystal is shown in Fig. 6. The plot shows that the photo current is increasing with the voltage applied and is found to be less than that of the dark current. This shows that the grown crystal exhibit negative photo conductivity [11].

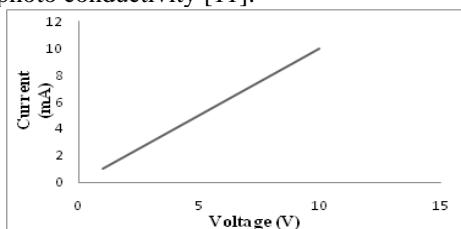


Fig. 6 PhotoConductivity of L-Histidinium Maleate

3.7 Photoluminescence Studies

Photoluminescence study is a nondestructive method of analysing the electronic structure of materials. The photoluminescence spectrum of the grown crystal was recorded in the range from 200 to 500 nm is shown in Fig. 7. The maximum intensity peak at 385nm corresponds to near band-edge excitons of as-grown crystals. Hence the grown crystals can be useful for UV filters and optoelectronic laser devices.

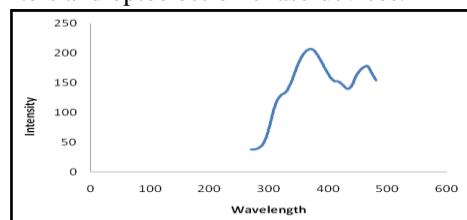


Fig.7 Photoluminescence spectrum of L-Histidinium Maleate
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3.7 Second Harmonic Generation

SHG of the material was found by Kurtz-powder technique[12]. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation ($\lambda=532$ nm) from the crystal. The KDP sample was used as the reference material and the second harmonic generation intensity of L-Histidinium Maleate was found to be 1.5 times that of KDP.

4. Conclusion

Single crystals of L-Histidinium Maleate were grown by the solvent evaporation technique in an aqueous solution at room temperature. Powder X-ray diffraction studies confirm the crystallinity of the grown crystal. The crystal belongs to the triclinic system. The optical absorption spectrum shows that the transparency cut off wavelength is 285nm. The material is thermally stable up to 101.6°C. The crystal exhibit negative photo conductivity. Photoluminescence study was carried out. The second harmonic generation intensity was found to be 1.5 times higher than that of KDP.

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